ZINC-SUBSTITUTED ZEOLITE ADSORBENTS AND PROCESSES FOR THE USE THEREOF IN GAS SEPARATION

Field of the Invention

5   The invention relates to a novel group of zeolite adsorbents containing divalent atoms in the framework to generate higher charge density frameworks containing more non-framework cations relative to composition structures with only trivalent or higher valent atoms
10   and processes for using such novel adsorbents having enhanced adsorption properties for gases, such as nitrogen.

BACKGROUND OF THE INVENTION

15   The separation of mixtures of gases, especially air, by so-called pressure swing adsorption processes is well-known to those skilled in gas separation technology. In principle, a PSA process involves the following steps:

20   (a) contacting a gaseous feed mixture of two or more different gases with an adsorbent under a first, relatively high, pressure, thereby causing at least one of the gases to be selectively adsorbed into the adsorbent, and producing a gaseous first product
25   mixture containing a greater proportion of the less selectively adsorbed gas or gases than the feed mixture;

         (b) separating the first product mixture from the adsorbent; and

30   (c) reducing the pressure on the adsorbent to a second pressure lower than the first pressure, thereby causing desorption from the adsorbent sieve of a

gaseous second product mixture containing a greater proportion of the selectively adsorbed gas(es) than the first mixture.

In industrial practice, PSA processes tend to be considerably more complicated than this simple description would suggest, and may involve one or more adsorption vessels usually referred to as "beds". Prior art describes PSA processes using multi-bed systems.

PSA processes represent an alternative method for oxygen separation from other gases to large-scale fractional distillation. In many PSA processes, zeolites are the preferred adsorbents because of their high adsorption capacity and their good selectivity. Both these properties are due, in part, to the microporous nature of zeolite structures, in which a large number of pores and cages of a consistent size extend throughout the lattice framework and cations occupy well-defined and consistent positions in the pores and cages. Most of these cations occupy hidden sites in the zeolite and are not accessible to gas molecules. However, for some compositions, a significant fraction of non-framework cations may be accessible to gas phase molecules. Non-bonded interactions of these active (exposed) cations with nitrogen molecules are responsible for the equilibrium nitrogen selectivity of low silica zeolites. The prior art attempted to increase nitrogen selectivity by employing various types of non-framework cations with low silica zeolites such as LTA, FAU, and EMT. These three letter codes recommended by the International zeolite Association refer to various zeolite

structures, e.g., FAU for zeolite X, Y and mineral faujasite. These codes refer to how framework atoms are connected to one another in each structure, rather than to actual chemical composition.

5   For example, U.S. Patent 2,882,243 by Milton describes the use of zeolite A having a silica/alumina ratio of 1.85±0.5 and containing hydrogen, ammonium, alkali metal, alkaline earth metal or transition metal cations as an adsorbent for separating nitrogen and

10   oxygen. U.S. Patent 2,882,244 also to Milton describes a similar process but in which X is a different type of zeolite having a silica/alumina ration of 2.5±0.5.

       U.S. Patent 3,140,933 to McKee describes the use of zeolite X which has been ion-exchanged with alkali

15   or alkaline earth metal cations as adsorbents for separating nitrogen and oxygen. Nitrogen adsorption performance improves when some of the sodium cations are replaced with lithium cations.

       U.S. Patent 4,925,460 discloses a process for

20   separating a gas mixture comprising components with different heats of adsorption, such as nitrogen from air, employing lithium-exchanged chabazite having a Si/Al ratio from 2.1 to 2.8 and at least 65% of the exchangeable cation capacity in the lithium form.

25   U.S. Patent 5,562,756 discloses a EMT structure with a Si/Al ratio less than 2.0 and a lithium cation exchange of at least 80%, preferably including an intergrowth with a FAU structure, where the EMT structure content is between 5 and 100%, for

30   selectively adsorptive separating nitrogen from oxygen.

U.S. Patent 5,413,625 discloses a lithium-alkaline earth metal X and A zeolites containing specific molar ratios of lithium to alkaline earth metal and to the use of these materials in separating nitrogen and

5 oxygen from mixtures thereof, especially air, by pressure swing adsorption (PSA) processes.

U.S. Patent 5,616,170 and European patent application EP 0758561A1 discloses chabazite, offretite, erionite, levyne, mordenite, gmelinite,

10 zeolite A, zeolite T, EMC-2, ZSM-3. ZSM-18, ZK-5, zeolite L and zeolite beta whose exchangeable cations are composed of 95 to 50% lithium and trivalent cations as preferentially adsorbing nitrogen from gas mixtures.

U.S. Patent 5,997,841 and European patent

15 application EP 0895966A1 disclose the FAU structure zincoaluminosilicates as novel gas separation adsorbents, particularly for separating oxygen from nitrogen in air.

EP 0 476 901 A2 discloses a zinc substitution in

20 the frameworks of zeolites with main channel size >0.22nm and Si/Al molar ratio <124.1.

In the prior art, the nitrogen selectivity was increased by lowering the Si/Al ratio of the zeolite frameworks and deploying non-framework cations with

25 high charge-to-radius ratios. The prior art compositions are limited by the $Si/Al \geq 1$ in accordance with Loewenstein's rule which forbids Al-O-Al linkages in zeolite frameworks. Si/Al = 1.0 already corresponds to the lowest Si/Al ratio possible. In the Li-form of

30 zeolite X (Si/Al = 1.0), only 32 out of 96 cations per unit cell (cubic symmetry) are located in the exposed sites III and III'. The other 64 lithium cations are

located in the hidden sites I' and II. Despite the
fact that the active cations in zeolite LiX(1.0) amount
to only 1/3 of the total cations, LiX(1.0)(SiO_2/Al_2O_3 =
2.0 or Si/Al = 1.0) displays the best performance at
5   ambient conditions among known zeolites.

      One object of the present invention is to increase
the number of exposed and active cations beyond that
corresponding to the SiAl = 1.0 zeolites in order to
further improve their nitrogen selectivity.

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SUMMARY OF THE INVENTION

The invention relates to a novel aluminosilicate
zeolite adsorbent comprising a molecular structure
containing at least one monovalent and/or divalent atom
15   substituted for at least one trivalent or higher valent
atom so that at least one exposed and active non-
framework charge balancing cation is increased in the
structure to effect higher selective gas (nitrogen)
selectivity over that of a similar molecular structure
20   having only trivalent atoms or higher valent atoms.
The invention also relates to a process for selectively
adsorbing nitrogen from a gas mixture, such as air,
containing nitrogen and at least one less strongly
adsorbent component which comprises contacting the gas
25   mixture with a zone of an adsorbent which is selective
for the adsorption of nitrogen, selectively adsorbing
nitrogen in the adsorbent and passing the gas mixture
less the adsorbent nitrogen out of the zone wherein the
adsorbent comprises an aluminosilicate zeolite material
30   containing a molecular structure containing at least
one monovalent and/or divalent atom substituted for at
least one trivalent or higher valent atom so as to

increase at least one exposed and active non-framework charge balancing cation to effect higher nitrogen selectivity over that of a similar molecular composition having only trivalent atoms or higher

5   valent atoms.

One embodiment of the present invention relates to the preparation of novel zeolite adsorbents which contain divalent framework atoms, i.e. Zn, instead of trivalent Al, and which possess superior separation

10 efficiency for oxygen separation due to higher number of active non-framework cations. In zeolite terminology, if an atom is connected to four other atoms via oxygen bridges forming a so-called 4-connected tetrahedral net, such an atom is termed a

15 framework atom and the bridging oxygen is termed framework oxygen. Typically, non-framework cations are those that balance the framework charge and are located in the cages or pores of zeolites, such as LiX(1.0) $(SiO_2/Al_2O_3 = 2.0$ or $Si/Al = 1.0)$, and are responsible

20 for the observed nitrogen adsorption selectivity. It was discovered that the substitution of divalent elements, such as zinc (Zn^{2+}), for the framework atoms (Al^{3+}) in low silica zeolites would result in higher number of non-framework cations required for total

25 charge balance and, therefore, higher nitrogen selectivity provided that such substitution increases the amount of exposed cations. For example, consider a simplified empirical formula of the Li-form of any zeolite with $Si/Al = 1.0$ and if one Al^{3+} is substituted

30 by one Zn^{2+} in such a zeolite, one additional Li^+ is required for charge balance.

The current invention indicates a range of structures where introduction of Zn will improve the sorption behavior. The present invention is aimed at increasing the total number of non-framework cations.

5 For example, the structure and sorption properties of Li-EMT(1.0) (SiO_2/Al_2O_3 = 2.0), where 4 framework Al atoms were substituted by 4 Zn atoms, was produced. Hence, the unit cell composition $Li_{52}Zn_4Al_{44}Si_{48}O_{192}$ as compared to $Li_{48}Al_{48}Si_{48}O_{192}$ for the true unit cell of

10 LiEMT(1.0). This structure is provided only as an example, and the invention relates to any aluminosilicate zeolite preferably with suitable structures containing 10 ring pores or greater and compositions with enough charge density to create

15 exposed cations.

Suitable adsorbents for this invention are selected from its group comprising EMT, EMT/FAU, BEA, CAN, GME, LTL, MAZ, MOR, MTW and OFF and from the group comprising Li-ZnEMT, Li-ZnEMT/FAU, Li-ZnBEA, Li-ZnCAN,

20 Li-ZnGME, Li-ZnLTL, Li-ZnMAZ, Li-ZnMOR, Li-ZnMTW and Li-ZnOFF.

The novel zeolite adsorbent would effectively allow the number of non-framework cations to increase beyond that permitted by the Lowenstein's rule for

25 aluminosilicate zeolite (Si/Al> or = 1.0) and thus the introduction of divalent elements at the same Si/M ratio equal to Si/Al would effectively overcome the current Si/Al synthesis limit for other zeolites, for instance, zeolite beta is currently synthesized at

30 Si/Al>5.

Preferably, the divalent atoms for the invention is zinc although cobalt, iron, magnesium, manganese,

beryllium or the like, could be used. Monovalent atoms
could also be used as substitutes for trivalent and/or
higher valent atoms to effectively increase the exposed
non-framework charge balancing cations. Preferably,

5   the novel divalent-substituted zeolite adsorbents for
this invention may contain at least 8 ring pores or
more, preferably 10 ring pores or greater.

Brief Description of the Drawings.

10   Figure 1 is a sketch of a molecular structure of
zeolite EMT.

Figure 2 is a graph of the relationship between
exposed Li and EMT framework compositions (true unit
cell).

15   Figure 3 is a graph of N_2 and O_2 isotherms of
adsorption on zeolites LiEMT and Li-ZnEMT(1.0) at 300K.

Figure 4 is a graph of N_2/O_2 ratio (selectivity)
for zeolites LiEMT and Li-ZnEMT(1.0) at 300K.

Detailed Description of Embodiments of The Invention

20   The zeolite EMC-2 that was used in the structure
and sorption modeling for our examples has an EMT
structure (Figure 1). EMT can be viewed as a hexagonal
version of FAU. The EMT structure is built from so-
called sodalite cages connected via double 6-rings to

25   form a three dimensional pore system. EMT has a large
channel (12-ring). The 6-ring opening of sodalite
cages are too small for small gas molecules such as
nitrogen and oxygen to penetrate. In addition, there
are 3 general cations sites, I', II, and III/III', in

30   the case of LiEMT. Only Li in sites III/III' are
accessible to gas molecules and these sites are

responsible for the large capacity and good
selectivity. Considerable experimental and molecular
modeling evidence indicates that the 48 Li cations in
the true unit cell are equally distributed among sites

5   I', II and III/III' in the EMT structure (96 cations
per expanded unit cell).

A good parent zeolite should have medium to high
charge density where exposed cations are present before
some Al is replaced by divalent species. Here,

10   "parent" describes a composition (hypothetical or real)
where the divalent atom locations are occupied by
aluminum The term "parent" does not imply that the
parent is a precursor to the adsorbent containing
framework divalent atoms. One reason for bringing

15   charge density and exposed cations into this invention
is that an earlier definition does not work all the
time since it failed to recognize the importance of
increasing the number of exposed cations. For example,
(see Figure 2) the substitution of Zn into the EMT

20   zeolite framework will increase the framework negative
charge density, and more non-framework cations will be
required (e.g. Li^+) to balance the charges. Only after
the number of Li^+ reaches the critical values (32 for
the true unit cell of EMT, 64 for the expanded unit

25   cell), the Li^+ begin to occupy the exposed site (Site
III for EMT) and the adsorbents show significant
improvement in nitrogen adsorption capacity. The
adsorbents with high Al and Zn contents can have higher
charge density than those of aluminosilicate zeolite

30   adsorbents, even the adsorbents with Si/Al=1.0. The
charge density of aluminosilicate zeolites has a limit
since the zeolite framework compositions are limited by

the Si/Al $\geq$ 1 in accordance with Loewenstein's rule which forbids Al-O-Al linkages in zeolite frameworks. Si/Al = 1.0 already corresponds to the lowest Si/Al ratio possible.

5   The present invention describes a novel group of zeolite adsorbents preferably with divalent atoms in the framework, which have improved nitrogen adsorption properties. These adsorbents were selected by molecular modeling techniques which predicted their

10 adsorption properties. The reliability of the current molecular modeling approaches have been validated by comparing structures and sorption properties of reference LiX structures to the corresponding experimental data.

15   The molecular modeling approach consisting of the following:

   A.   Adopt the previously validated sorption forcefield, containing parameters for zeolite framework oxygen-gas molecules and non-

20   framework Li gas molecule van der Waals interactions, as well as the partial charges on zeolite and gas molecules.

   B.   Use validated theoretical structures of hypothetical adsorbents, e.g., framework Zn

25   substituted zeolite Li-EMT.

   C.   Perform Grand Canonical Monte Carlo modeling of nitrogen/oxygen sorption for these hypothetical adsorbents.

   The following examples are provided to illustrate

30 the adsorbents of the present invention.

EXAMPLE 1

Lithium-exchanged zeolite EMT and zeolite EMT
containing framework Zn^{2+} atoms

The structure for the zeolite EMT framework was
taken from an experimental study by Ch. Baerlocher,
L.B. et al. (Microporous Materials 2 (1994) 269). For
sorption simulation accuracy and convenience, the
hexagonal cell of EMT (composition $Li_{48}Al_{48}Si_{48}O_{192}$ for
Si/Al = 1.0 material) was transformed to an
orthorhombic cell having the composition $Li_{96}Al_{96}Si_{96}O_{384}$
(expanded unit cell). Sites I' and II are the most
stable and fully occupied (32 cations each) in the EMT
structure. The remaining 32 Li^+ cations are located in
the exposed sites III/III' in accordance with the
experimental and modeling data. The theoretical limit
of 48 active cations may be achieved only when an
additional 16 cations (48-32=16) are required to
balance the higher negative charge on the framework for
the expanded unit cell.

Li^+ cations located in sites III/III' are
responsible for the high nitrogen capacity and
selectivity of the zeolite. Here, a practical path is
described to increasing the negative framework charge
leading to increased number of Li cations in the
exposed site III/III' and higher nitrogen selectivity
as compared with zeolite EMT(1.0).

According to the model, 8 framework Al^{3+} atoms
were randomly substituted with 8 Zn^{2+} atoms in the
structure EMT 1.0. The overall unit cell composition
can be represented by $Li_{104}Zn_8Al_{88}Si_{96}O_{384}$ [so-called Li-
ZnEMT(1.0)]. Li^+ locations in sites I' and II were
previously assigned (see above). The task of locating

40 remaining Li cations (32+8) is described in detail below.

LOCATION OF NON-FRAMEWORK SPECIES

5   Charges and van der Waals parameters were assigned to each framework atom in accordance with the augmented cvff_aug forcefield validated for aluminosilicates (Insight II 4.0.0 program, Molecular Simulations Inc., San Diego, 1996). The Li^+ cations in this forcefield

10   have formal charges, while the framework atoms had the following charges: O=-1.2, Zn=+0.4, Si+2.4, and Al=+1.4. The charge on the zinc atoms was assigned to achieve electrical neutrality. Also, since the van der Waals parameters for Zn^{2+} atom are not defined in the

15   cvff_aug forcefield, the assumption is made that they are identical to those of Al^{3+} atoms. This assumption is justified because both Al^{3+} and Zn^{2+} are rather small atoms with low polarizability and high effective charge. Therefore, Li^+-Al^{3+}/Zn^{2+} interactions are

20   dominated by long-range electrostatic forces, and the van der Waals forces provided only minor contribution to the total interaction energy at relevant internuclear separations. A three-dimensional host reference grid with grid spacing of ca.0.5Å was created

25   commensurate with the framework symmetry. The Li^+ cation-framework non-bond electrostatic and repulsive-dispersive interactions were calculated at each grid point using the Eward summation method and a short range 5.5Å cutoff, respectively. A second, so-called

30   Li^+ cation reference grid of identical dimensions was constructed, a single Li^+ cation place at its origin, and the interaction of a second Li^+ cation at each grid

point was computed. A Li$^+$ cation was placed in the
framework at the lowest energy position found in the
preceding step, i.e. during computation of the Li$^+$
cation-framework interaction. Since the framework
contained an additional Li$^+$ cation, the reference grid
was updated by superimposing it with the Li$^+$ cation
reference grid, centered abut the location of the
recently added Li$^+$ cation. The lowest energy position
was again determined and populated. These steps were
repeated until all Li$^+$ cations were added to the EMT
framework.

LATTICE ENERGY MINIMIZATION

The Li$^+$ cation locations were then optimized using
GULP energy minimization program using the BFGS
minimiser and appropriate atomic penitential (Gale,
J.D. J. Chem. Soc., Faraday Trans., 1997, 93, 629).

TABLE 1

Li cation site occupancies in expanded unit cells of
Li-EMT(1.0), Li-EMT(1.09) and Li-ZnEMT(1.0)

Site	Site I'	Site II	Site III (and Site III'
Li-EMT(1.0)	32	32	32
Li-EMT(1.09)	32	32	24
Li-ZnEMT(1.0)	32	32	40

Molecular modeling confirmed the expectations of
much higher number of exposed Li cations occupying
sites III/III' in the structure of Li-ZnEMT(1.0) than
in LiEMT(1.0) (Table 1). The effect of the higher
number of exposed Li cations on the adsorption behavior
of this model system using a Metropolis Grand Canonical
Monte Carlo method is shown below in Example 2.

EXAMPLE 2

Monte Carlo Sorption of Single Component Isotherms
of Adsorption of Oxygen and Nitrogen on Zeolites
5 LiEMT(1.0), LiEMT(1.09) and Li-ZnEMT(1.0).

The Monte Carlo Sorption method has been described
in detail in A.J. Richards, K. Watanabe, N. Austin and
M.R. Stapleton, Journal of Porous Material, 1995, 2,
43. In this method, nitrogen and oxygen molecules are
10 randomly placed into the unit cell of a zeolite and the
interaction energy between these molecules and zeolite
is calculated. Nitrogen and oxygen molecules are then
added, deleted, moved and rotated a very large number
of times (>3,000,000 per pressure point). This is done
15 to adequately sample the configuration space of the
system and equalize the chemical potential of the
molecules inside the zeolite pores with that of the gas
phase. The average number of nitrogen and oxygen
molecules inside the micropores after a large number of
20 steps corresponds to their equilibrium sorption
capacity. Some zeolites contain large regions of the
unit cell, which may be occupiable, but inaccessible to
gas molecules. The common procedure is to block such
inaccessible regions of the unit cell as the sodalite
25 cages in zeolite EMT, by placing large dummy atoms at
their centers. These regions are then excluded from
the simulation, with the simulation itself not being
affected in any other aspect. The modeled adsorption
of N_2 and O_2 in zeolites LiEMT(1.0) and Li-ZnEMT(1.0)
30 at 300K was made using such fashion.

The simulated isotherms of adsorption for
LiEMT(1.0), LiEMT(1.09) and Li-ZnEMT(1.0) are compared

with the experimental sorption data for these zeolites
in Figures 3 and 4 and shown in Table 2.

TABLE 2

5 Simulated single component isotherms of N_2 and O_2
adsorption on zeolites LiEMT and Li-ZnEMT(1.0) at 300K.

	26.7 kPa			100 kPa			225 kPa		
	N_2 mol/ uc*	O_2 mol/ uc	$N_2/$ O2	N_2 mol/u c	O_2 mol/ uc	N_2/O_2	N_2 mol/ uc	O_2 mol/ uc	N_2/O_2
LiEMT (1.09)	5.80	0.42	13.81	17.02	1.61	10.57	28.28	3.37	8.39
LiEMT (1.0)	8.36	0.45	18.58	20.57	1.64	12.54	32.80	3.51	9.34
Li-Zn EMT (1.0)	12.87	0.40	32.18	24.19	1.51	16.02	34.53	3.11	11.10

*molecules per expanded unit cell of EMT containing 192
tetrahedral atoms.

10   The sorption model adequately predicts sorption
behavior of existing zeolites (Figures 3 and 4) and
thus it confirms that both the sorption capacity and
nitrogen selectivity (expressed as the ratio of the
single component loading of N_2 and O_2 at the special
15 pressure) is proportional to the number of active
cations located in sites III/III' for zeolite Li-
EMT(1.0). The sorption model further indicated
superior nitrogen sorption and selectivity of the
framework Zn-substituted zeolite LiEMT(1.0) when
20 compared to LiEMT(1.0). This superior nitrogen
selectivity is due to the presence of additional Li^+
cations in sites III'. These additional Li^+ cations
are required to balance the extra negative framework
charge resulting from the substitution of divalent Zn^{2+}
25 for Al^{3+} atoms into the framework of zeolite EMT(1.0).

According to the adsorption data shown in Table 2 and Figures 3 and 4, the N_2/O_2 selectivity at 225 kPa is ca. 19% higher for zeolite Li-ZnEMT(1.0) than LiEMT1.0. Based on theoretical predictions of cation

5 locations and sorption data, it is believed that the higher nitrogen selectivity of the Li-ZnEMT(1.0) system resulted from the higher number of exposed and active Li^+ cations located in the zeolitic supercages near sites III'.

10

EXAMPLE 3

The framework Zn substitution creates an additional non-framework charge that does not necessarily lead to improved sorption properties in all

15 tetrahedral frameworks. This example describes a situation where framework Zn substitution does not improve sorption properties. The reasons for such behavior are explained below.

Consider a unit cell of zeolite LiEMT at Si/Al=

20 5.32 with Li cations occupying sites I' and II located inside the hexagonal prisms connecting sodalite cages and the 6R of the sodalite cages, respectively. It is both experimentally observed and confirmed by molecular modeling that sites I' are inaccessible to gas

25 molecules, while the sites II are accessible, but inactive as sorption sites. Sites II are inactive in sorption due to the presence of the framework atoms in their vicinity which cancel the strong electrostatic interaction of the Li cations with the gas molecules.

30 Consider next a Li-ZnEMT structure at Si/(Al+Zn)=5 with Zn/Al=1. This corresponds to adding another 16 Li cations per full unit cell of EMT. These additional Li

cations now completely fill sites I' (32 total), and the remaining 16 Li cations populate sites II, i.e. the 6R windows of the sodalite cages. Therefore, despite the fact that the Li cation content increased by 50%, sorption properties of this zeolite system remained virtually unchanged.

The following are some of the conclusions from the examples:

1.   According to the sorption model, nitrogen sorption and selectivity of zeolite Li-EMT is proportional to the number of sites III/III' Li^+ cations;

2.   Substitution of divalent metal atoms, such as Zn, into the framework of zeolite EMT(1.0) would introduce additional non-framework cations into the exposed cation sites III';

3.   The model Li-ZnEMT(1.0) system displayed higher N_2/O_2 selectivity as compared to LiEMT(1.0) due to proportionately higher number of sites III/III' Li^+ cations;

4.   Substitution of divalent metal atoms for higher valent atoms in tetrahedral frameworks is a general approach to increase active non-framework cation content and improve separation efficiency of gases with different polarity or quadrupole moment by adsorption methods, such as nitrogen from oxygen in air by PSA.

Obviously, many modifications and variations of the present invention are possible in light of the above. Thus, it is to be understood that, within the scope of the appended claims, this invention may be

practiced otherwise than as specifically described above.